

SUPPORTING INFORMATION

Copper(I) Catalyzed Asymmetric 1,2-Addition of Grignard Reagents to α -Methyl α,β -Unsaturated Ketones

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General Information

Flash chromatography: Merck silica gel type 9385 230-400 mesh, TLC: Merck silica gel 60, 0.25 mm. Components were visualized by UV and Seebach's reagent, a mixture of phosphomolybdic acid (25 g), cerium (IV) sulfate (7.5 g), H₂O (500 mL) and H₂SO₄ (25 mL) or potassium permanganate staining. Progress and conversion of the reaction were determined by GC-MS (GC, HP6890; MS HP5973) with an HP1 or HP5 column (Agilent Technologies, Palo Alto, CA). High resolution mass spectra (HRMS) were recorded on a AEI-MS-902 and FTMS orbitrap (Thermo Fisher Scientific) mass spectrometer. ¹H- and ¹³C-NMR were recorded on a Varian AMX400 (400 and 100.59 MHz, respectively) or a Varian Gemini 200, using CDCl₃ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (CHCl₃: δ 7.26 for ¹H, δ 77.0 for ¹³C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. Carbon assignments are based on APT ¹³C-NMR experiments. Optical rotations were measured on a *Schmidt + Haensch* polarimeter (Polartronic MH8) with a 10 cm cell (*c* given in g/100 mL). Enantiomeric excesses were determined by HPLC analysis using a Shimadzu LC-10ADVP HPLC equipped with a Shimadzu SPD-M10A VP diode array detector or by capillary GC analysis (HP 6890, CP-Chiralsil-Dex-CB column (25 m x 0.25 mm) or Chiraldex B-PM (30 m x 0.25 mm x 0.25 μm)) using a flame ionization detector.

All reactions were carried out under a nitrogen atmosphere using oven dried glassware and using standard Schlenk techniques. *t*BuOMe and dichloromethane were dried and distilled from calcium hydride; toluene, THF and *n*-hexane were dried and distilled from sodium. All copper salts were purchased from Aldrich, and used without further purification. Starting materials were prepared following literature procedures.^{1,2} Grignard reagents were purchased from Aldrich (*i*BuMgBr (2 M in Et₂O), EtMgBr (3 M in Et₂O), *n*-PentylMgBr (2 M in Et₂O). Ligands **L1-L5** were purchased from Aldrich. Racemic products were synthesized by reaction of the α,β-unsaturated ketones (**1**) and the corresponding Grignard reagent at rt in Et₂O. All Grignard reagents were prepared from the corresponding alkyl bromides and Mg activated with I₂ in Et₂O.

¹ Lu, S.-M., Bolm, C. *Angew. Chem., Int. Ed.* **2008**, *47*, 8920.

² Moser, R., Boskovic, Z. V., Crowe, C. S., Lipshutz, B. H. *J. Am. Chem. Soc.* **2010**, *132*, 7852.

General procedures for the copper-catalyzed 1,2-addition of Grignard reagents.

Procedure A: addition to α -substituted α,β -unsaturated ketones

A Schlenk tube equipped with septum and stirring bar was charged with $\text{CuBr}\cdot\text{SMe}_2$ (0.015 mmol, 3.08 mg, 5 mol%) and ligand **L5** (0.018 mmol, 6 mol%). Dry *t*BuOMe (3 mL) was added and the solution was stirred under nitrogen at room temperature for 15 min. Corresponding ketone (0.3 mmol in 1 mL *t*BuOMe) was added and the resulting solution was cooled to $-78\text{ }^\circ\text{C}$. The corresponding Grignard reagent (0.36 mmol, 1.2 eq, in Et_2O) added to the reaction mixture over 15 min. Once the addition was complete, the reaction mixture was monitored by TLC and GCMS. The reaction was quenched by the addition of MeOH (1 mL) and saturated aqueous NH_4Cl (2 mL). The mixture was warmed to room temperature, diluted with Et_2O and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 5 mL) and the combined organic layers were dried with anhydrous Na_2SO_4 , filtered and the solvent was evaporated *in vacuo*. The crude product was purified by flash chromatography on silica gel using mixtures of *n*-pentane and Et_2O as the eluent.

Note: Gas chromatography analysis was carried out to determine the 1,2-addition, 1,4-addition and 1,2-reduction ratio on a sample obtained after aqueous workup and extraction with Et_2O , which was passed through a short plug of silica gel to remove copper residues.

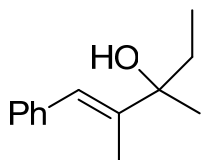
Procedure B: addition to α -substituted α,β -unsaturated ketones

A Schlenk tube equipped with septum and stirring bar was charged with $\text{CuBr}\cdot\text{SMe}_2$ (0.015 mmol, 3.08 mg, 5 mol%) and ligand **L5** (0.018 mmol, 6 mol%). Dry *t*BuOMe (3 mL) was added and the solution was stirred under nitrogen at room temperature for 15 min. Then, corresponding ketone (0.3 mmol in 1 mL *t*BuOMe) was added and the resulting solution was cooled to $-78\text{ }^\circ\text{C}$. In a separate Schlenk, the corresponding Grignard reagent (0.36 mmol, 1.2 eq) was diluted with *t*BuOMe (combined volume of 1 mL) under nitrogen and added dropwise to the reaction mixture over 3 hours using a syringe pump. Once the addition was complete, the reaction mixture was monitored by TLC and GCMS. The reaction was quenched by the addition of MeOH (1 mL) and saturated aqueous NH_4Cl (2 mL) and the mixture was warmed to room temperature, diluted with Et_2O and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 5 mL) and the combined organic layers were dried with anhydrous Na_2SO_4 , filtered and the solvent was evaporated *in vacuo*. The crude product was purified by flash chromatography on silica gel using mixtures of *n*-pentane and Et_2O as the eluent.

Procedure C: addition to α -substituted α,β -unsaturated ketones

A Schlenk tube equipped with septum and stirring bar was charged with $\text{CuBr}\cdot\text{SMe}_2$ (0.015 mmol, 3.08 mg, 5 mol%) and ligand **L5** (0.018 mmol, 6 mol%). Dry *t*BuOMe (3 mL) was added and the solution was stirred under nitrogen at room temperature for 15 min. Then, corresponding ketone (0.3 mmol in 1 mL *t*BuOMe) was added and the resulting solution was cooled to $-60\text{ }^\circ\text{C}$. The corresponding Grignard reagent (0.36 mmol, 1.2 eq, in Et_2O) was diluted with *t*BuOMe (combined volume of 1 mL) under nitrogen and added to the reaction mixture over 15 min. Once the addition was complete, the reaction mixture was monitored by TLC and GCMS. The reaction was quenched by the addition of MeOH (1 mL) and saturated aqueous NH_4Cl (2 mL) and the mixture was warmed to room temperature, diluted with Et_2O and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 5 mL) and the combined organic layers were dried with anhydrous Na_2SO_4 , filtered and the solvent was evaporated *in vacuo*. The crude product was purified by flash chromatography on silica gel using mixtures of *n*-pentane and Et_2O as the eluent.

(+)-(E)-2,3-Dimethyl-1-phenylpent-1-en-3-ol (3a):



Using method **A**: Reaction was performed with ligand *ent*-**L5** and EtMgBr. Colorless oil obtained as a 97:2:1 mixture of **3a**, **4a**, and **5a** after column chromatography (SiO₂, *n*-pentane:Et₂O 90:10), **3a** [95% yield, 70:30 *e.r.*].

¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.29 (m, 2H), 7.26 – 7.17 (m, 3H), 6.65 (s, 1H), 1.83 (s, 3H), 1.70 (m, 2H), 1.48 (s, 1H), 1.40 (s, 3H), 0.88 (t, *J* = 7.4, 3H).

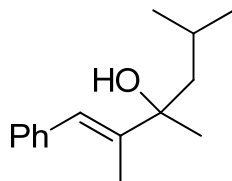
¹³C NMR (101 MHz, CDCl₃) δ 143.06, 138.61, 129.03, 127.99, 126.07, 123.67, 76.21, 33.02, 27.39, 14.59, 8.10.

[α]_D²⁰ = +2.2 (*c* = 0.8, CHCl₃).

HRMS (ESI+, *m/z*): calcd for C₁₃H₁₈O-OH [M-OH]⁺: 173.1331; found: 173.1337.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, detection at 240 nm, retention times (min): 23.8(major) and 24.9(minor).

(+)-(E)-2,3,5-Trimethyl-1-phenylhex-1-en-3-ol (**3b**):



Using method **B**: Reaction was performed with ligand *ent*-**L5** and *i*BuMgBr. Colorless oil obtained as a 97:1:2 mixture of **3b**, **4b**, and **5b** after column chromatography (SiO₂, *n*-pentane:Et₂O 90:10), **3b** [93% yield, 92:8 *e.r.*].

¹H NMR (400 MHz, CDCl₃) δ 7.33 (t, *J* = 7.6, 2H), 7.26 – 7.17 (m, 3H), 6.70 (s, 1H), 1.83 (s, 3H), 1.7 (s, 1H), 1.59 – 1.55 (d, *J* = 6.4, 2H), 1.47 (m, 1H), 1.40 (s, 3H), 0.98 (d, *J* = 6.6, 3H), 0.93 (d, *J* = 6.6, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.54, 138.55, 129.00, 128.00, 126.05, 123.16, 76.56, 48.89, 28.99, 24.42, 24.35, 15.07.

[α]_D²⁰ = +8.0 (*c* = 0.5, CHCl₃).

HRMS (ESI+, *m/z*): calcd for C₁₅H₂₂O-OH [M-OH]⁺: 201.1644; found: 201.1649.

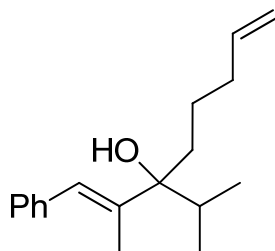
Enantiomeric ratio was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, detection at 240 nm, retention times (min): 16.7(major) and 20.3(minor).

The same above reaction performed by using method **A**: Colorless oil obtained as a 96:2:2 mixture of **3b**, **4b**, and **5b** after column chromatography (SiO₂, *n*-pentane:Et₂O 90:10), **3b** [92% yield, 91:9 *e.r.*].

Reaction on 1.5 mmol scale:

The same above reaction was performed by using method **B** on 1.5 mmol scale: Colorless oil was obtained as a 95:1:4 mixture of **3b**, **4b**, and **5b** after column chromatography (SiO₂, *n*-pentane:Et₂O 90:10), **3b** [90% yield, 92:8 *e.r.*].

(+)-(E)-3-Isopropyl-2-methyl-1-phenylocta-1,7-dien-3-ol (3c):



Using method A: Reaction was performed with ligand **L5** and pent-4-en-1-ylmagnesium bromide. Colorless oil obtained as a 98:0:2 mixture of **3c**, **4c**, and **5c** after column chromatography (SiO₂, *n*-pentane:Et₂O 90:10), **3c** [95% yield, 83:17 *e.r.*].

¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.29 (m, 2H), 7.26 – 7.16 (m, 3H), 6.65 (s, 1H), 5.81 (m, 1H), 5.15 – 4.86 (m, 2H), 2.18 – 1.90 (m, 3H), 1.75 (s, 3H), 1.72 – 1.57 (m, 2H), 1.56 – 1.41 (m, 1H), 1.35 (s, 1H), 1.32 – 1.16 (m, 1H), 1.02 (d, *J* = 6.7, 3H), 0.86 (d, *J* = 9.8, 3H).

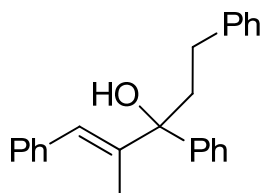
¹³C NMR (101 MHz, CDCl₃) δ 141.24, 138.81, 138.63, 129.03, 128.01, 125.99, 124.79, 114.60, 79.93, 36.25, 34.13, 23.14, 17.11, 16.21, 15.09.

[α]_D²⁰ = +24.5 (*c* = 3.4, CHCl₃).

HRMS (ESI+, *m/z*): calcd for C₁₈H₂₆O-OH [M-OH]⁺: 241.1957; found: 241.1956.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, detection at 240 nm, retention times (min): 12.7(major) and 41.6(minor).

(-)-(E)-2-Methyl-1,3,5-triphenylpent-1-en-3-ol (3d):



Using method C: Reaction was performed with ligand **L5** and phenethylmagnesium bromide. Colorless oil obtained as a 86:12:2 mixture of **3d**, **4d**, and **5d** after column chromatography (SiO₂, *n*-pentane:Et₂O 90:10), **3d** [83% yield, 81:19 *e.r.*].

¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.48 (m, 2H), 7.43 – 7.27 (m, 9H), 7.25 – 7.09 (m, 4H), 6.95 (s, 1H), 2.69 (m, 2H), 2.56 – 2.35 (m, 2H), 1.92 (s, 1H), 1.71 (d, *J* = 1.1, 3H).

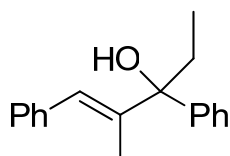
¹³C NMR (101 MHz, CDCl₃) δ 144.97, 142.54, 141.55, 138.02, 129.11, 128.46, 128.28, 128.10, 127.13, 126.40, 125.86, 124.96, 79.56, 41.11, 30.24, 15.09.

[α]_D²⁰ = -26 (*c* = 0.5, CHCl₃).

HRMS (ESI+, *m/z*): calcd for C₂₄H₂₄O-OH [M-OH]⁺: 311.1807; found: 311.1801.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, detection at 240 nm, retention times (min): 53.2(minor) and 55.3(major).

(-)-(E)-2-Methyl-1,3-diphenylpent-1-en-3-ol (3e):



Using method **A**: Reaction was performed with ligand **L5** and EtMgBr. Colorless oil obtained as a 95:3:2 mixture of **3e**, **4e**, and **5e** after column chromatography (SiO₂, *n*-pentane:Et₂O 90:10), **3e** [94% yield, 92:8 *e.r.*].

¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.46 (m, 2H), 7.41 – 7.26 (m, 7H), 7.26 – 7.19 (m, 1H), 6.89 (s, 1H), 2.31 – 2.07 (m, 2H), 1.82 (s, 1H), 1.66 (s, 3H), 0.94 (t, *J* = 7.3, 3H).

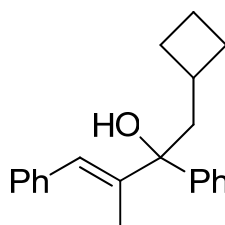
¹³C NMR (101 MHz, CDCl₃) δ 145.07, 141.72, 138.25, 129.09, 128.12, 128.05, 126.92, 126.28, 125.89, 124.76, 79.77, 31.38, 15.01, 7.91.

[α]_D²⁰ = -59.1 (*c* = 0.9, CHCl₃).

HRMS (ESI+, *m/z*): calcd for C₁₈H₂₀O-OH [M-OH]⁺: 235.1487; found: 235.1481.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, detection at 240 nm, retention times (min): 27.1(minor) and 31.4(major).

(-)-(E)-1-Cyclobutyl-3-methyl-2,4-diphenylbut-3-en-2-ol (3f):



Using method **C**: Reaction was performed with ligand **L5** and (cyclobutylmethyl)magnesium bromide. Colorless oil obtained as a 92:5:3 mixture of **3f**, **4f**, and **5f** after column chromatography (SiO₂, *n*-pentane:Et₂O 90:10), **3f** [87% yield, 88:12 *e.r.*].

¹H NMR (400 MHz, CDCl₃) δ 7.47 (dd, *J* = 13.0, 11.6, 2H), 7.38 – 7.28 (m, 6H), 7.25 – 7.18 (m, 2H), 6.86 (s, 1H), 2.46 (d, *J* = 8.6, 1H), 2.26 (m, 3H), 2.15 – 1.98 (m, 1H), 1.82 (s, 3H), 1.64 (t, *J* = 8.1, 3H), 1.55 (s, 1H).

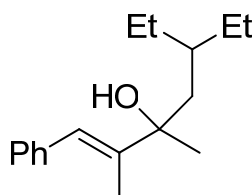
¹³C NMR (101 MHz, CDCl₃) δ 145.34, 142.17, 138.19, 129.52, 129.07, 128.55, 128.05, 128.04, 126.83, 126.26, 125.80, 124.29, 79.91, 45.96, 31.97, 30.02, 19.61, 15.12.

[α]_D²⁰ = -32.1 (*c* = 0.9, CHCl₃).

HRMS (ESI+, *m/z*): calcd for C₂₁H₂₄O-OH [M-OH]⁺: 275.1801; found: 275.1796.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, detection at 240 nm, retention times (min): 26.6(major) and 27.8(minor).

(-)-(E)-5-Ethyl-2,3-dimethyl-1-phenylhept-1-en-3-ol (3g):



Using method **A**: Reaction was performed with ligand **L5** and (2-ethylbutyl)magnesium bromide. Colorless oil obtained as a 97:1:2 mixture of **3g**, **4g**, and **5g** after column chromatography (SiO₂, *n*-pentane:Et₂O 90:10), **3g** [95% yield, 96:4 *e.r.*].

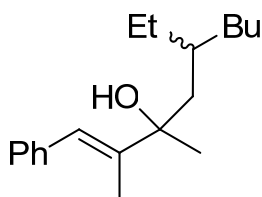
^1H NMR (400 MHz, CDCl_3) δ 7.33 (t, $J = 7.5$, 2H), 7.26 – 7.17 (m, 3H), 6.68 (s, 1H), 1.83 (s, 3H), 1.70 – 1.51 (m, 2H), 1.48 (s, 3H), 1.32 (m, 5H), 0.82 (t, $J = 7.2$, 3H), 0.71 (t, $J = 7.3$, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 143.55, 138.60, 129.00, 128.01, 126.03, 123.29, 76.53, 43.54, 36.29, 28.85, 26.46, 15.09, 10.84.
 $[\alpha]_{\text{D}}^{20} = -7.0$ ($c = 0.8$, CHCl_3).

HRMS (ESI+, m/z): calcd for $\text{C}_{17}\text{H}_{26}\text{O}-\text{OH}$ $[\text{M}-\text{OH}]^+$: 229.1957; found: 229.1963.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, detection at 240 nm, retention times (min): 15.8(minor) and 16.5(major).

(+)-(E)-5-Ethyl-2,3-dimethyl-1-phenylnon-1-en-3-ol (3h):



Using method **B**: Reaction was performed with ligand *ent*-**L5** and (2-ethylhexyl)magnesium bromide. Colorless oil obtained as a 99:0:1 mixture of **3h**, **4h**, and **5h** after column chromatography (SiO_2 , *n*-pentane:Et₂O 90:10), **3h** [96% yield, 1:1 dr, 96:4 *e.r.*].

^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.29 (m, 3H), 7.22 (dd, $J = 18.3$, 7.4, 2H), 6.68 (s, 1H), 2.47 (s, 1H), 1.83 (s, 3H), 1.59 (m, 3H), 1.47 – 1.36 (m, 6H), 1.35 – 1.16 (m, 5H), 0.86 (m, 6H).

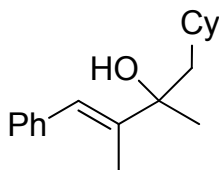
^{13}C NMR (101 MHz, CDCl_3) δ 143.58, 129.67, 129.00, 128.44, 128.00, 126.02, 123.29, 76.58, 76.54, 44.00, 34.85, 34.01, 33.92, 28.91, 28.88, 26.95, 23.09, 15.10, 14.13, 10.77.

$[\alpha]_{\text{D}}^{20} = +2.4$ ($c = 1.3$, CHCl_3).

HRMS (ESI+, m/z): calcd for $\text{C}_{19}\text{H}_{30}\text{O}-\text{OH}$ $[\text{M}-\text{OH}]^+$: 257.2270; found: 257.2264.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, detection at 240 nm, retention times (min): 11.8(major) and 12.7(minor).

(+)-(E)-1-Cyclohexyl-2,3-dimethyl-4-phenylbut-3-en-2-ol (3i):



Using method **A**: Reaction was performed with ligand *ent*-**L5** and (cyclohexylmethyl)magnesium bromide. Colorless oil obtained as a 99:1:0 mixture of **3i**, **4i**, and **5i** after column chromatography (SiO_2 , *n*-pentane:Et₂O 90:10), **3i** [95% yield, 94:6 *e.r.*].

^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.31 (m, 2H), 7.26 – 7.18 (m, 3H), 6.70 (s, 1H), 1.83 (s, 3H), 1.77 – 1.50 (m, 8H), 1.46 – 1.38 (s, 3H), 1.34 – 1.09 (m, 3H), 1.08 – 0.89 (m, 2H).

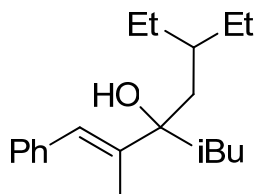
^{13}C NMR (101 MHz, CDCl_3) δ 143.62, 138.65, 129.01, 128.03, 126.04, 123.16, 76.55, 47.72, 35.08, 33.86, 28.94, 26.47, 26.32, 15.12.

$[\alpha]_{\text{D}}^{20} = +1.2$ ($c = 2.5$, CHCl_3).

HRMS (ESI+, m/z): calcd for $\text{C}_{18}\text{H}_{26}\text{O}-\text{OH}$ $[\text{M}-\text{OH}]^+$: 241.1957; found: 241.1952.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane/*i*-PrOH 99:1, 40 °C, detection at 240 nm, retention times (min): 22.4(minor) and 23.2(major).

(+)-(E)-6-Ethyl-2-methyl-4-(1-phenylprop-1-en-2-yl)octan-4-ol (3j):



Using method C: Reaction was performed with ligand *ent*-L5 and (2-ethylbutyl)magnesium bromide. Colorless oil obtained as a 96:1:3 mixture of **3j**, **4j**, and **5j** after column chromatography (SiO₂, *n*-pentane:Et₂O 97:03), **3j** [92% yield, 98:2 *e.r.*].

¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.29 (m, 3H), 7.26 – 7.17 (m, 2H), 6.73 (s, 1H), 2.10 – 2.01 (s, 1H), 1.77 (s, 3H), 1.74 – 1.55 (m, 3H), 1.54 – 1.21 (m, 7H), 1.07 – 0.92 (m, 6H), 0.89 – 0.76 (m, 6H).

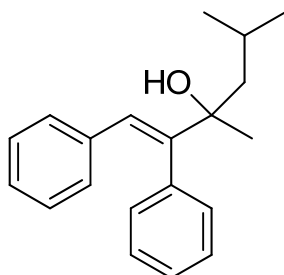
¹³C NMR (101 MHz, CDCl₃) δ 141.75, 138.79, 129.66, 128.97, 128.40, 128.02, 125.95, 124.41, 79.39, 49.33, 43.93, 35.64, 26.49, 24.57, 24.04, 15.78, 10.83.

[α]_D²⁰ = +1.9 (*c* = 1.3, CHCl₃).

HRMS (ESI+, *m/z*): calcd for C₂₀H₃₂O-OH [M-OH]⁺: 271.2426; found: 271.2420.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, detection at 240 nm, retention times (min): 10.3(major) and 10.9(minor).

(-)-(E)-3,5-Dimethyl-1,2-diphenylhex-1-en-3-ol (3k):



Using method C: Reaction was performed with ligand L5 and *i*BuMgBr. Colorless oil was obtained as a 84:12:4 mixture of **3k**, **4k**, and **5k** after column chromatography (SiO₂, *n*-pentane:Et₂O 90:10), **3k** [81% yield, 84:16 *e.r.*].

¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.28 (m, 3H), 7.15 (dd, *J* = 7.8, 1.6, 2H), 7.05 (dd, *J* = 5.2, 2.0, 3H), 6.87 (s, 1H), 6.81 (dd, *J* = 7.2, 2.5, 2H), 1.97 (m, 1H), 1.64 – 1.60 (dd, *J* = 14.5, 5.0, 2H), 1.50 (s, 1H), 1.40 (s, 3H), 1.00 (2d, *J* = 6.7, 6H).

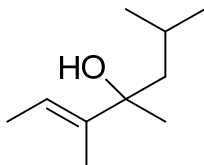
¹³C NMR (101 MHz, CDCl₃) δ 148.72, 139.28, 137.00, 129.83, 129.16, 128.49, 127.79, 127.10, 126.42, 125.47, 76.71, 49.18, 29.11, 24.74, 24.52.

[α]_D²⁰ = -19.1 (*c* = 0.7, CHCl₃).

HRMS (ESI+, *m/z*): calcd for C₂₀H₂₄O-OH [M-OH]⁺: 263.1801; found: 263.1794.

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, detection at 240 nm, retention times (min): 22.4(minor) and 24.0(major).

(-)-(E)-3,4,6-Trimethylhept-2-en-4-ol (3l):



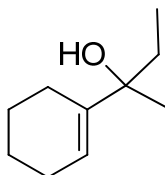
Using method **C**: Reaction was performed with ligand **L5** and *i*BuMgBr. Colorless oil was obtained as a 89:8:3 mixture of **3l**, **4l**, and **5l** after column chromatography (SiO₂, *n*-pentane:Et₂O 90:10), **3l** [85% , 74:26 *e.r.*].

The physical data were identical in all respects to those previously reported.³

$[\alpha]_D^{20} = -2.8$ ($c = 0.5$, CHCl₃).

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane/*i*-PrOH 100:00, 40 °C, detection at 240 nm, retention times (min): 18.9(minor) and 20.2(major).

(+)-2-(Cyclohex-1-en-1-yl)butan-2-ol (3m):



Using method **B**: Reaction was performed with ligand *ent*-**L5** and EtMgBr. Colorless oil obtained as a 87:12:2 mixture of **3m**, **4m**, and **5m** after column chromatography (SiO₂, *n*-pentane:Et₂O 90:10), **3m** [82% yield, 71:29 *e.r.*]. The physical data were identical in all respects to those previously reported.^{4,5}

$[\alpha]_D^{20} = +0.6$ ($c = 2.9$, MeOH), [lit.⁶ (51% ee): $[\alpha]_D^{20} = +0.7$ ($c = 3.0$, MeOH)].

Enantiomeric ratio was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, detection at 215 nm, retention times (min): 14.3(major) and 15.2(minor).

³ Caporusso, A. M., Giacomelli, G., Lardicci, L. *J. Org. Chem.* **1982**, *47*, 4641.

⁶ Caporusso, A. M.; Giacomelli, G.; Lardicci, L. *J. Org. Chem.* **1982**, *47*, 4640.

⁴ Ramón D. J., Yus, M. *Tetrahedron* **1998**, *54*, 5651.

⁵ Weber, B., Seebach, D. *Tetrahedron* **1994**, *50*, 6117.

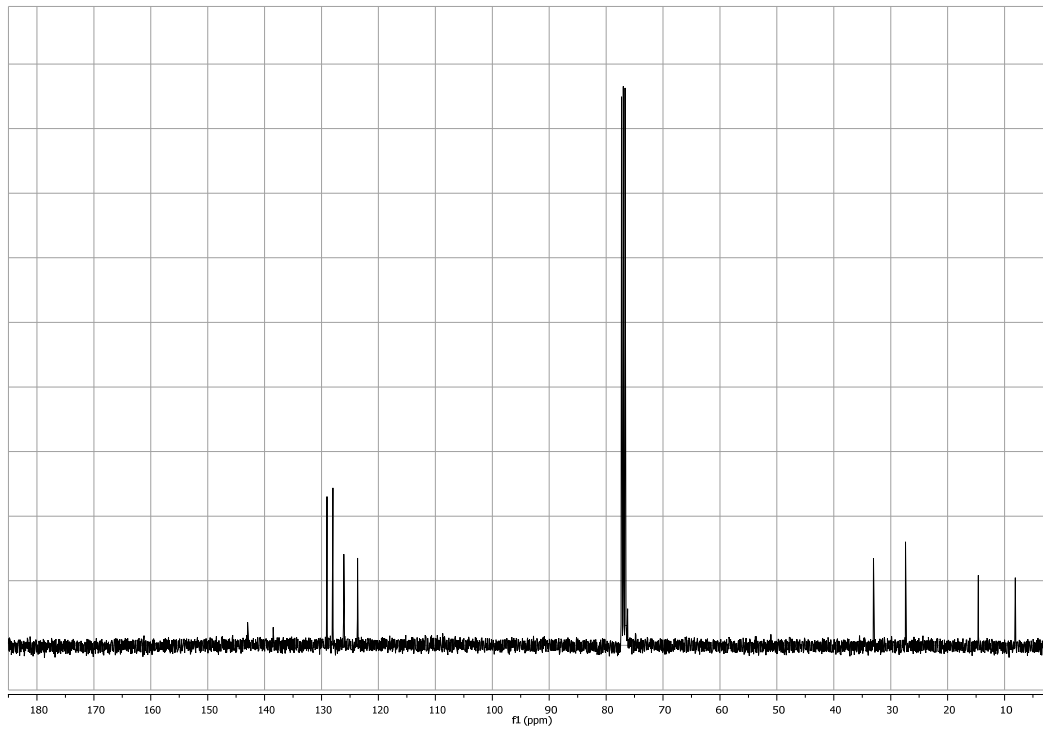
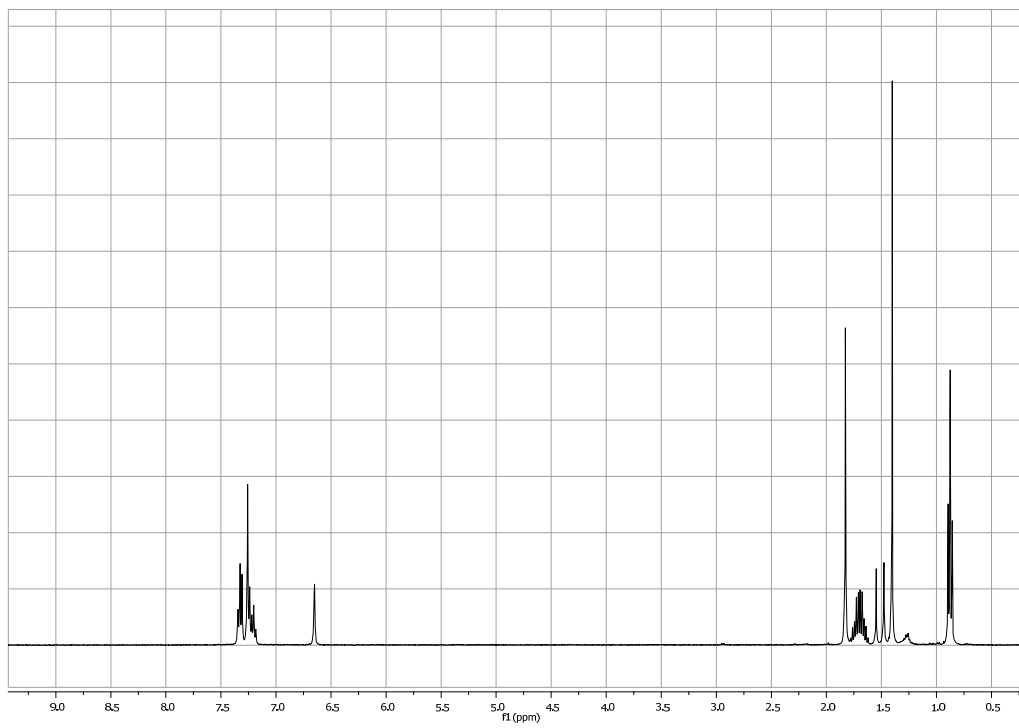
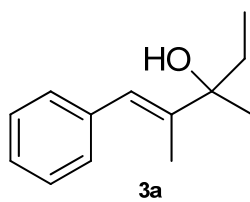
NMR spectra of all new compounds

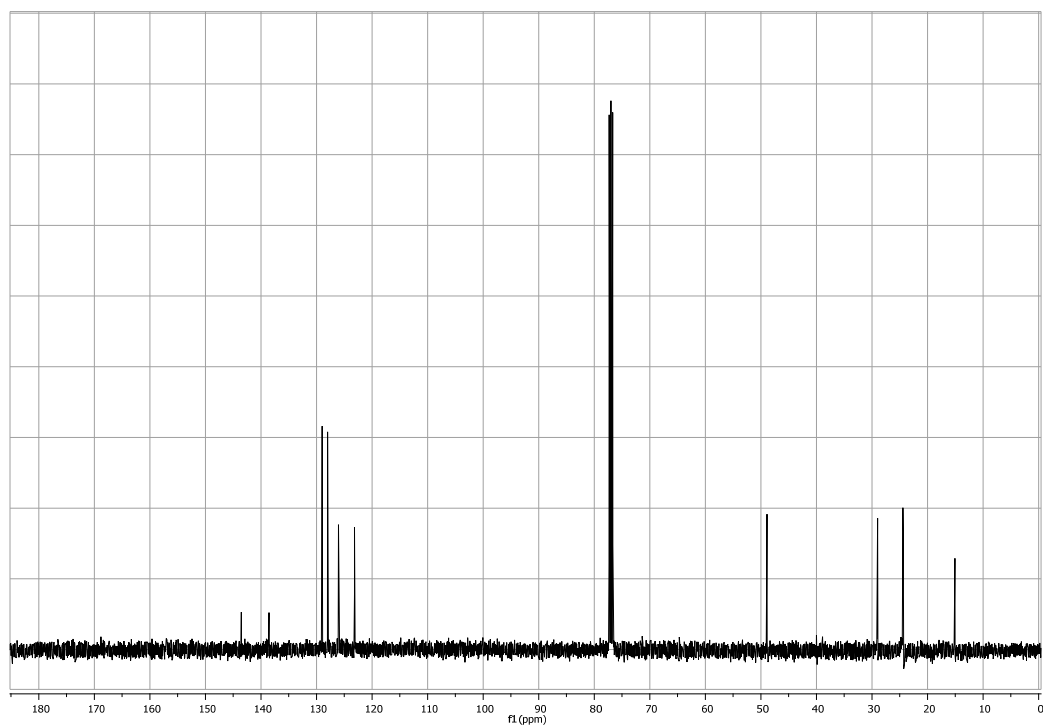
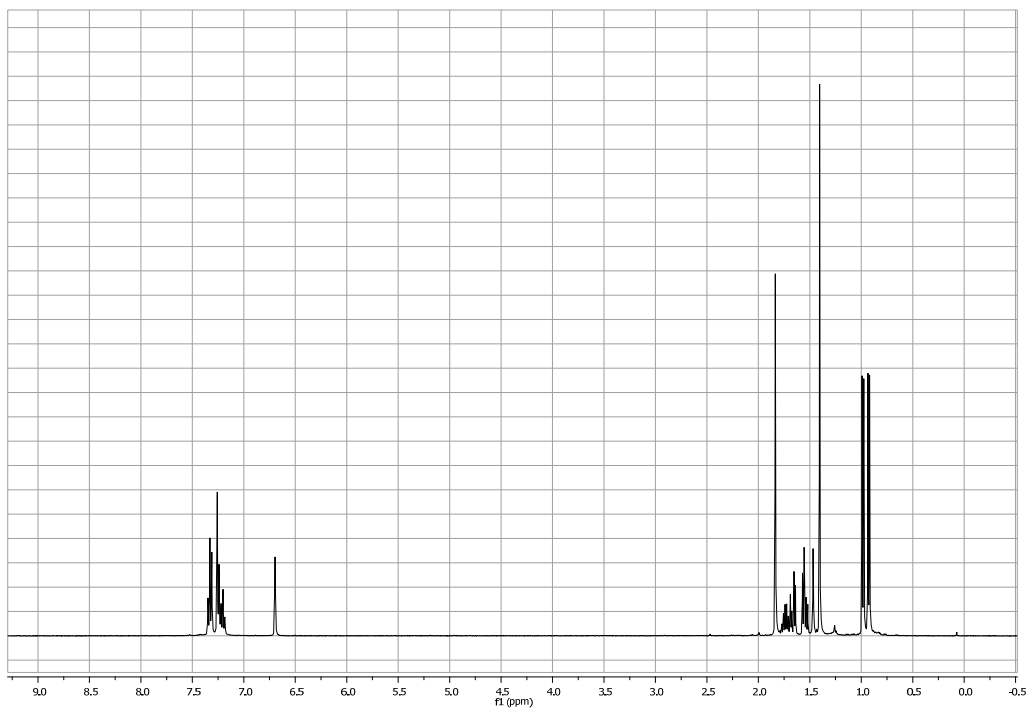
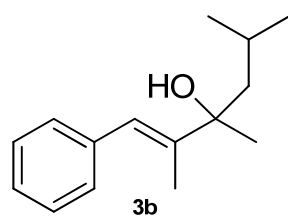
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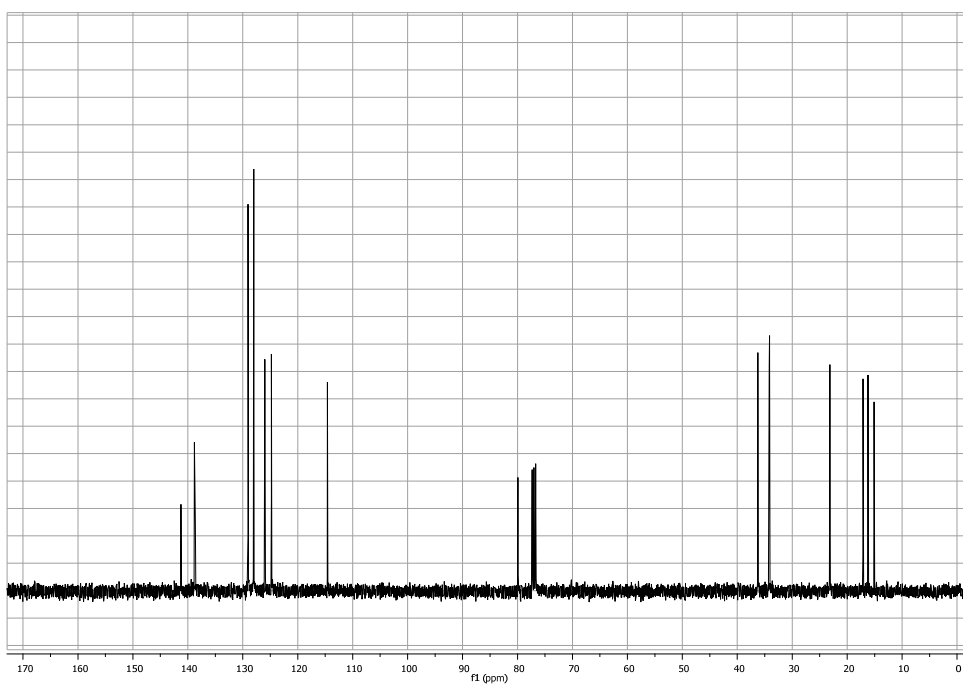
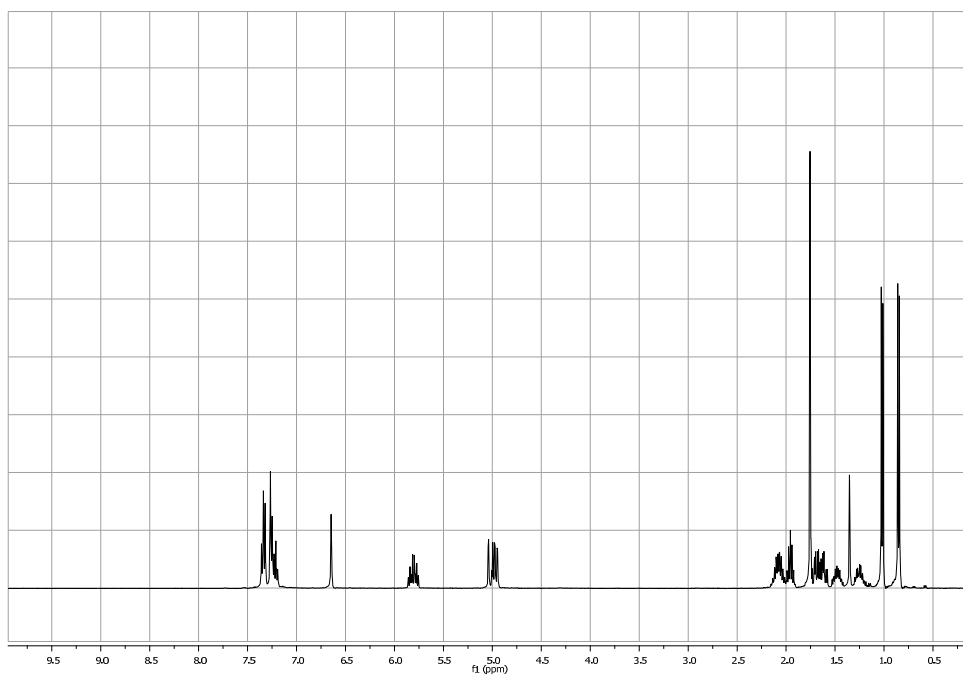
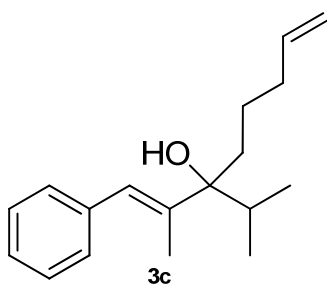
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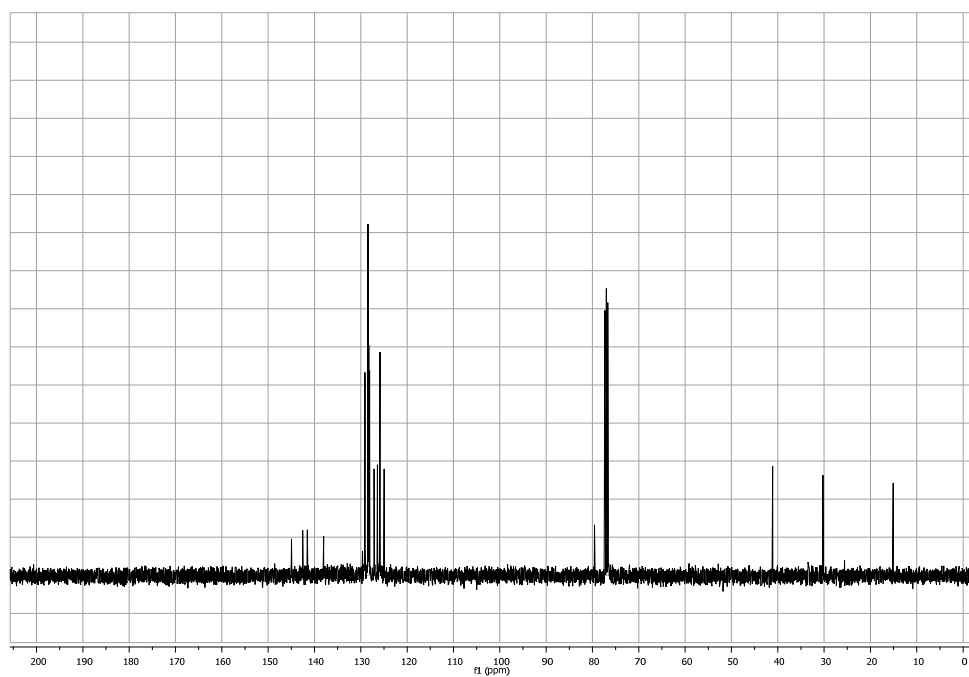
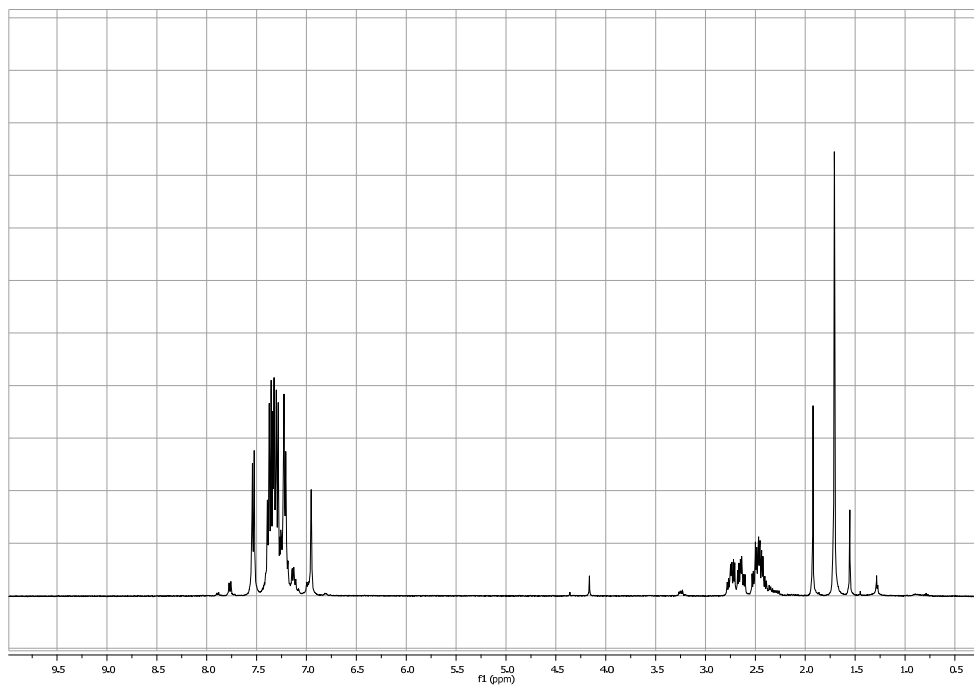
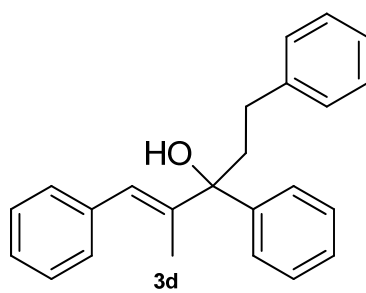
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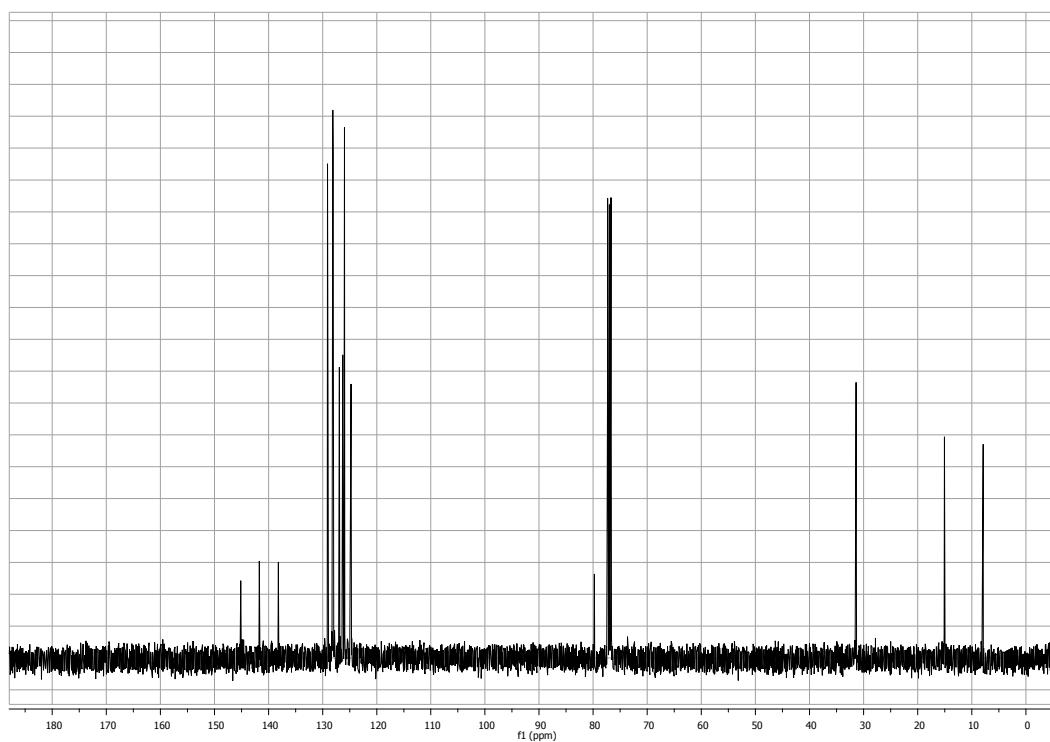
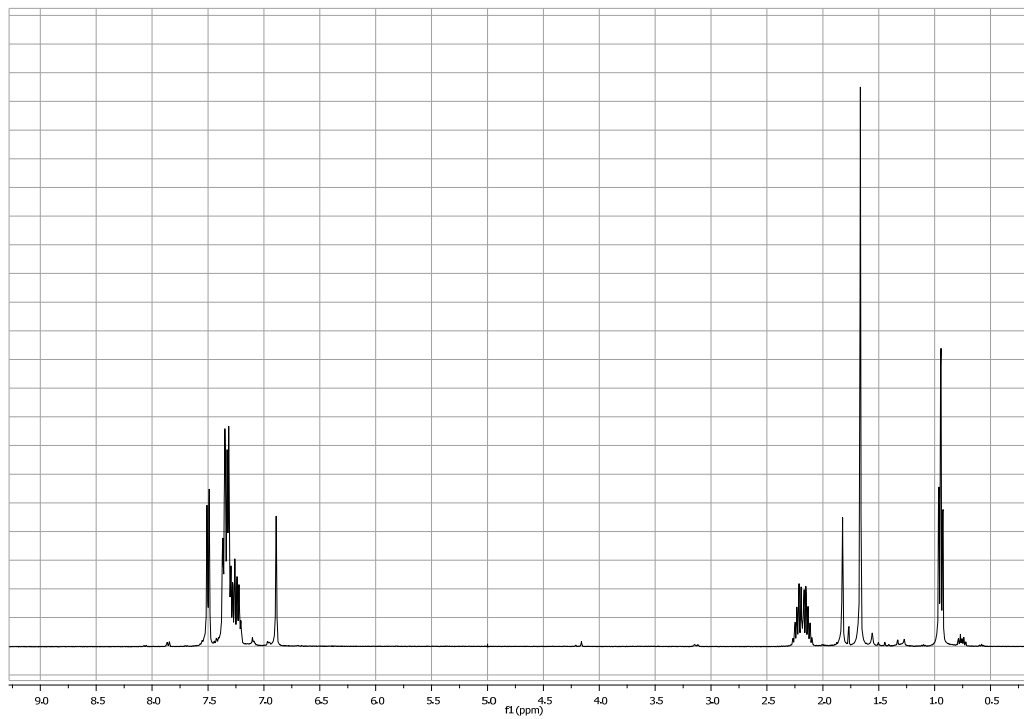
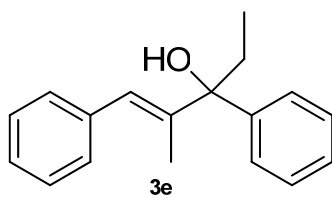
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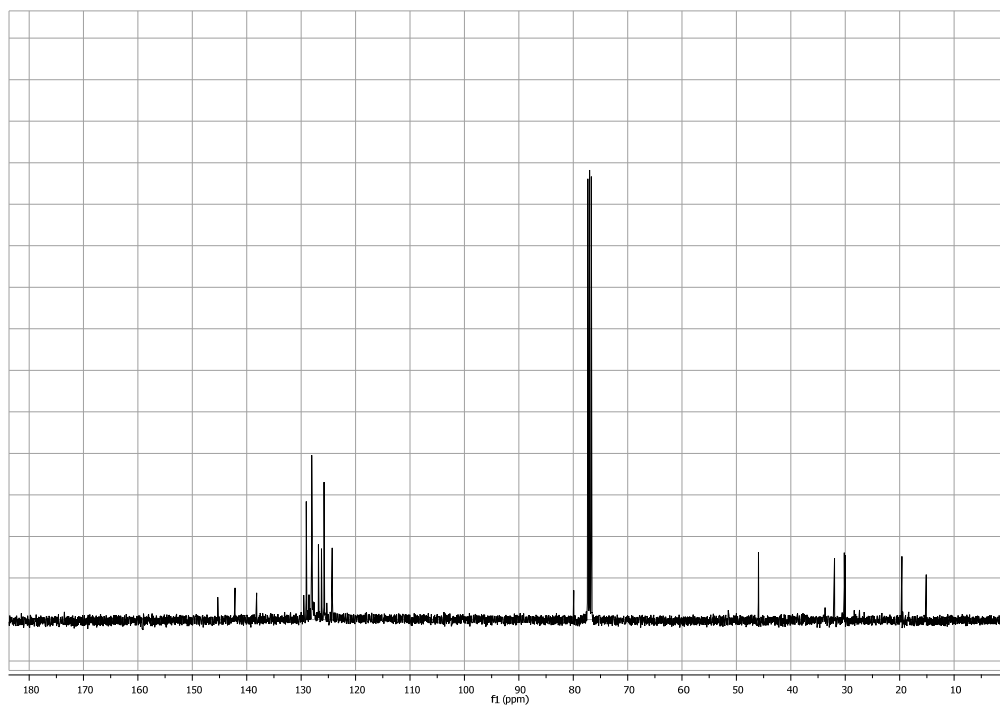
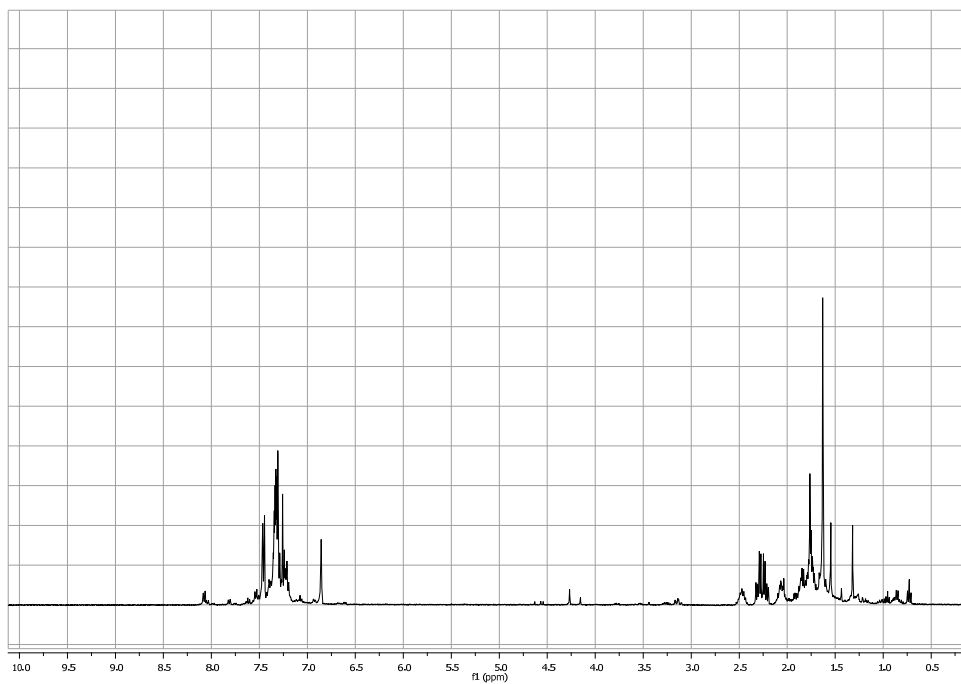
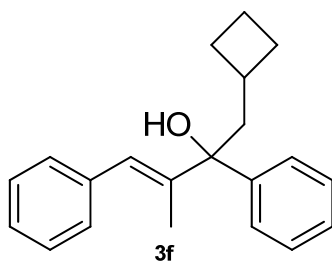


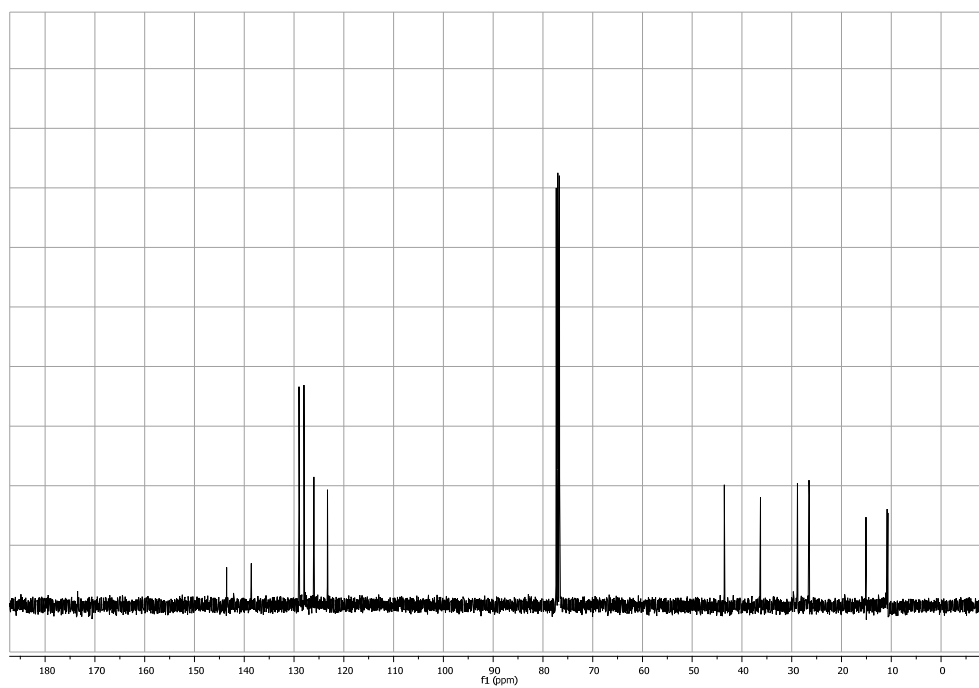
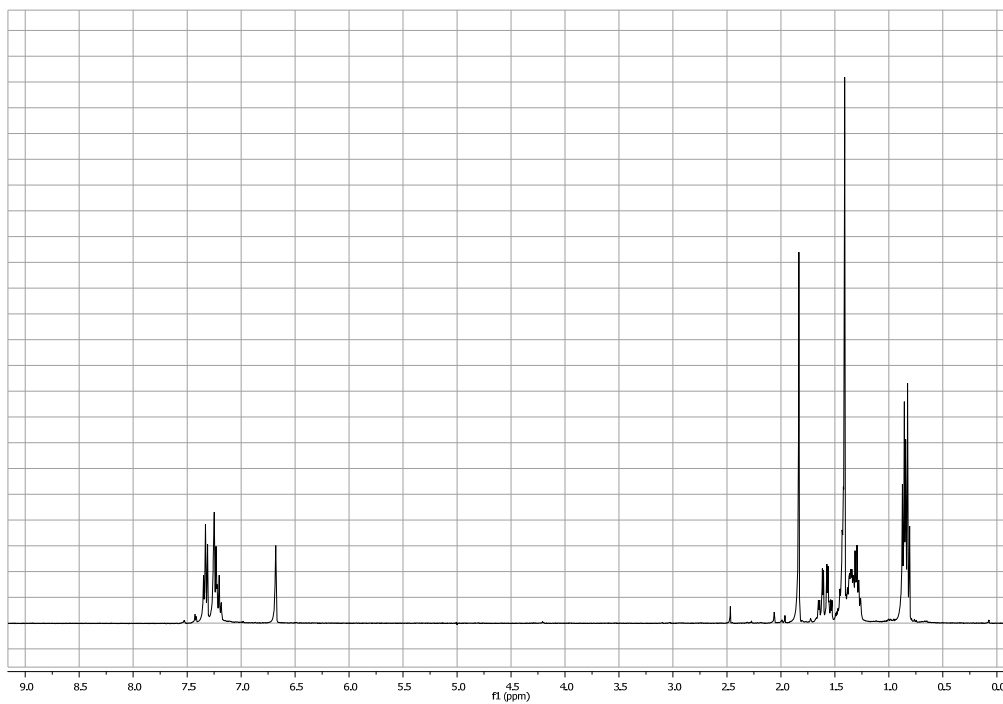
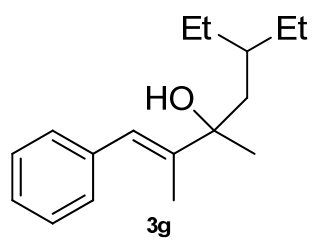


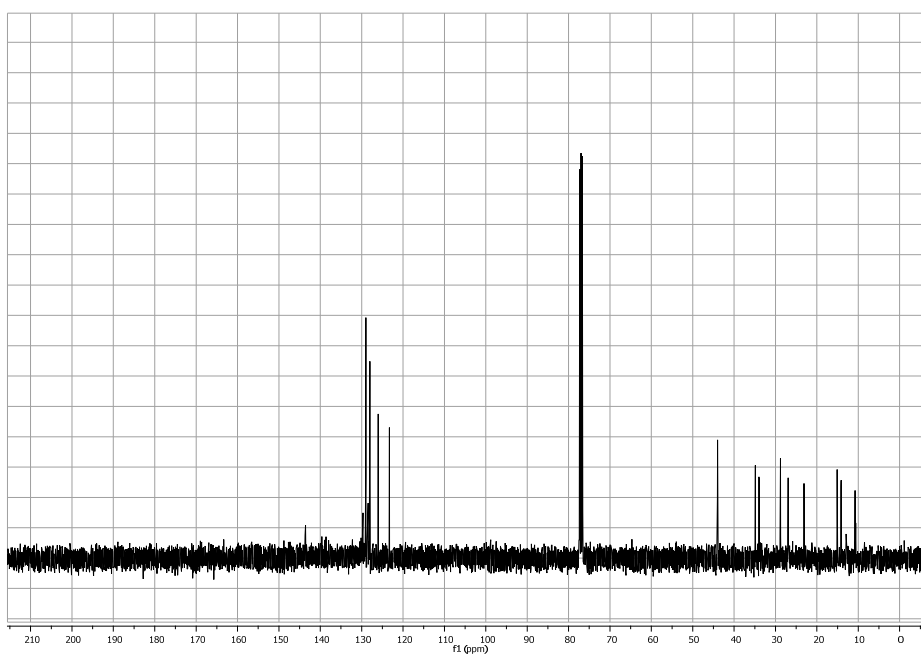
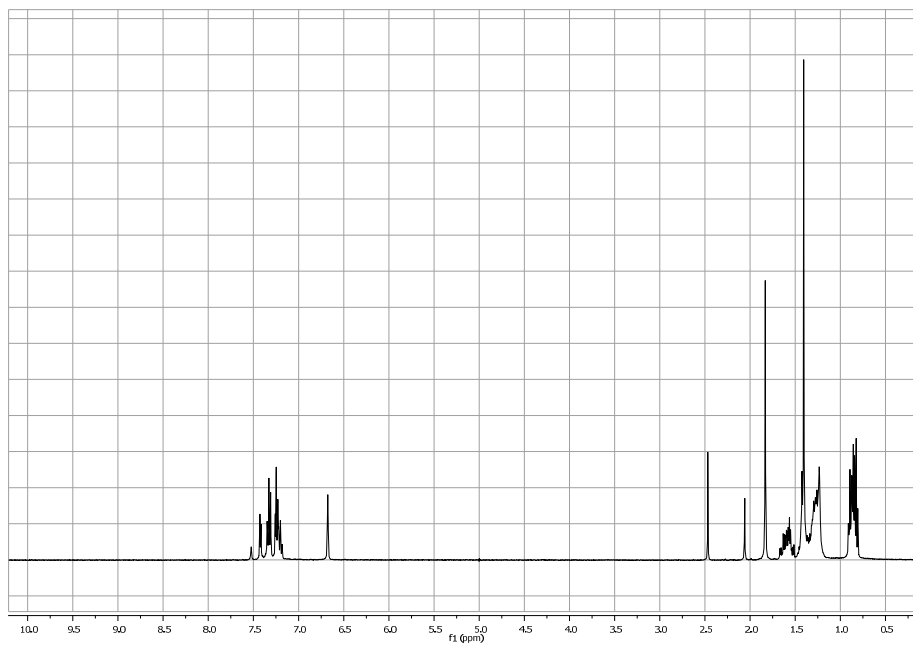
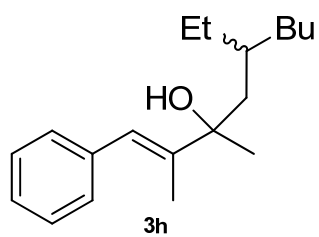


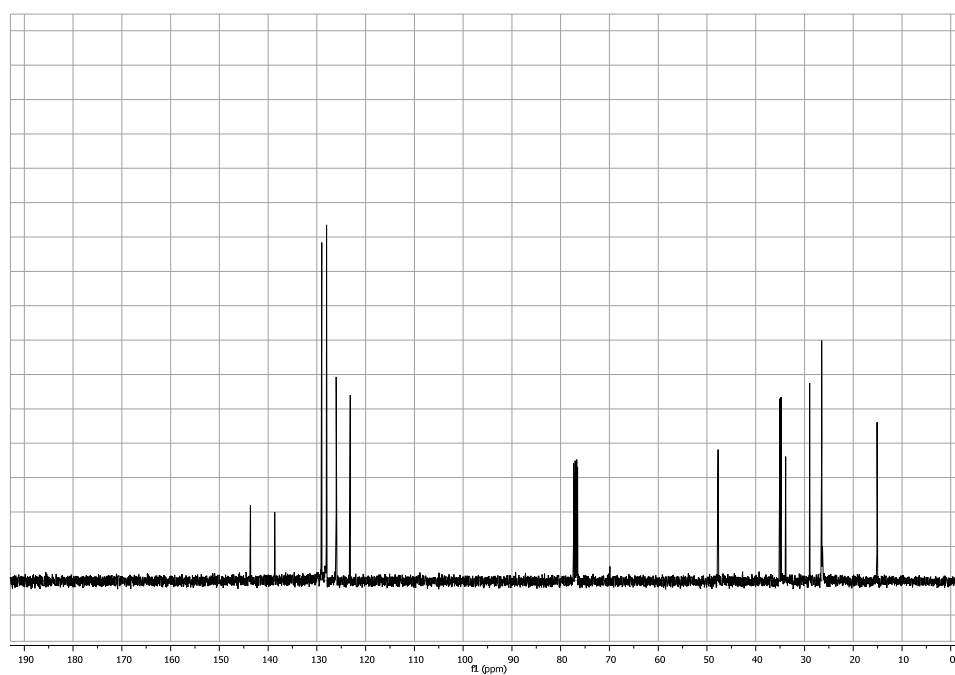
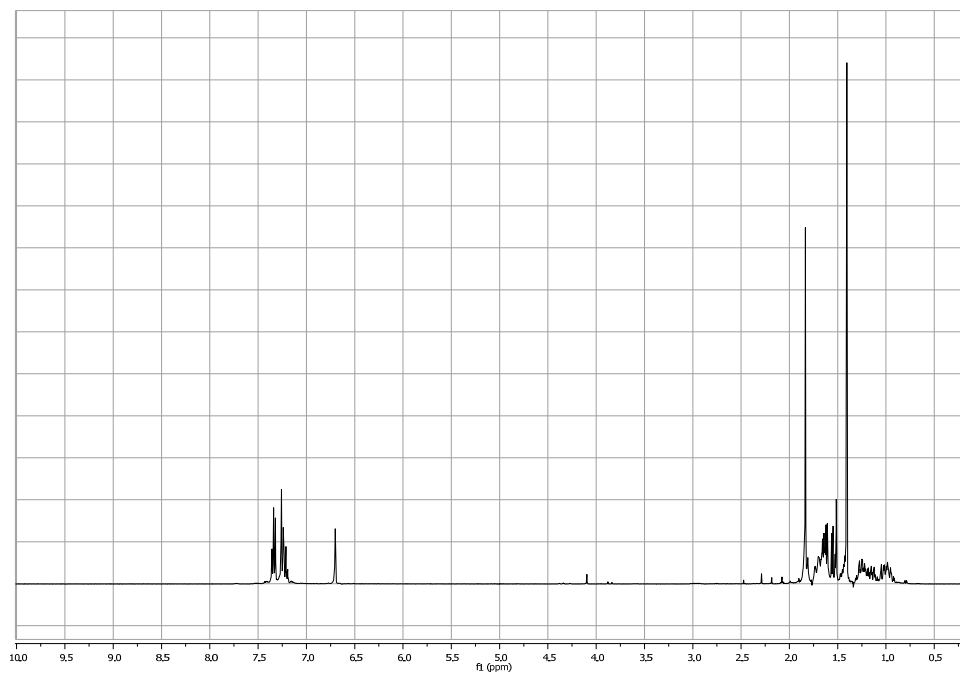
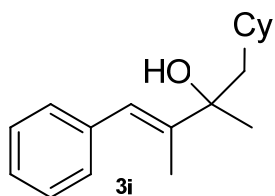


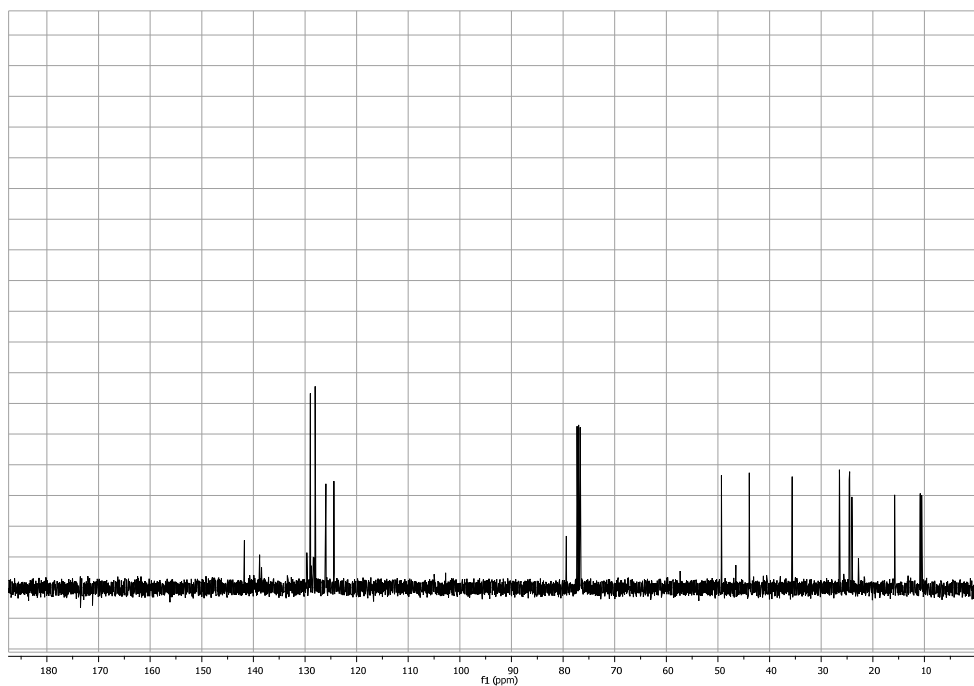
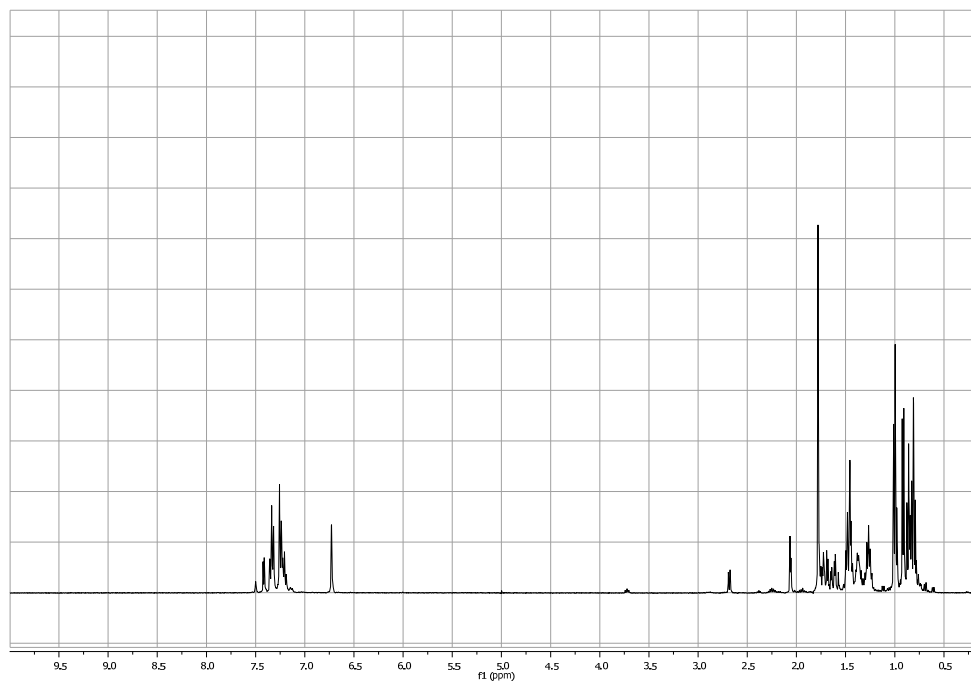
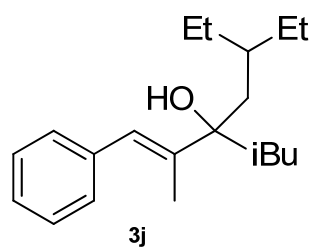


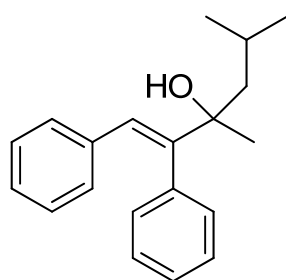












3k

